Solution combustion synthesis: From powders to coatings

Dr. S.T. Aruna
Surface Engineering Division
CSIR-National Aerospace Laboratories
Bangalore – 560 017

aruna_reddy@nal.res.in

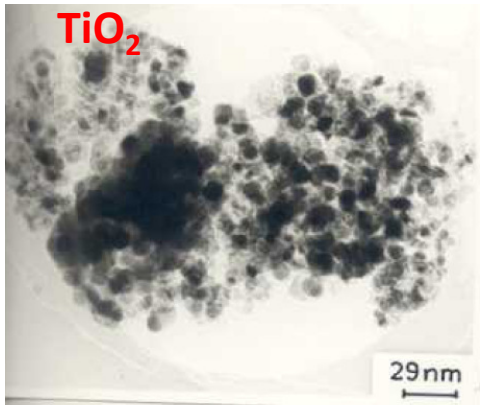
Commemoration of 25 years of SCS
@IPC, IISc, 12th July 2013

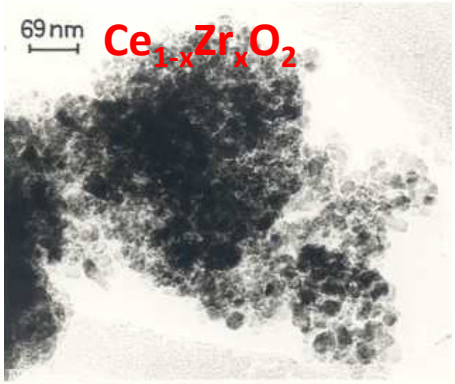
Outline

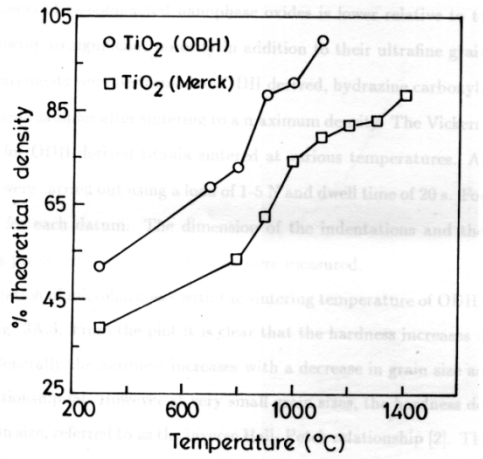
- **My work @ IPC**
- **Mixture of fuels approach**
- **Powders to coatings**
  - ***Wear & corrosion resistant electrodeposited MMCs***
  - ***Solid oxide fuel cells***
  - ***Thermal barrier coatings (TBCs)***
  - ***Solar selective coatings***
  - ***Corrosion resistant sol-gel coatings***
- **Concluding remarks**

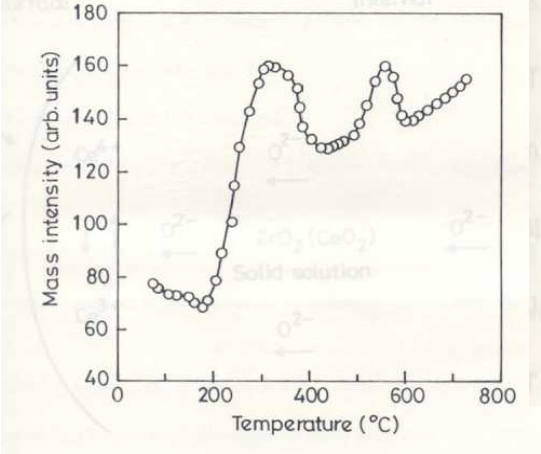
Work @ IPC (1994-1997)

- I Part – Nanosize TiO_2, Ceria-zirconia, ferrites









Particle shape, size and hysteresis properties of $BaFe_{12}O_{19}$ obtained by different routes

Sample	Particle shape (nm)	Particle size (μm)	M_s (emu/g)	M_r (emu/g)	H_c (Oe)
Ceramic	platelet	1-4	78.2	39.4	2178
Nitrates decomposition	platelet	0.15-0.6	70.2	34.3	4320
Liquid mix technique	spherical	0.1-0.15	74.9	36.2	5550
Pyrolysis citrate	spherical	0.03-0.05	73	35.5	5340
Pyrolysis nitrate	spherical	0.03-0.04	70.7	34.5	4867
Combustion	spherical	0.03-0.04	84	41.3	4697

Journal of Materials Synthesis and Processing 1996, 4, 175-180, citations 56

Nanostructured materials 1998, 10 (6), 955-964, citations 84

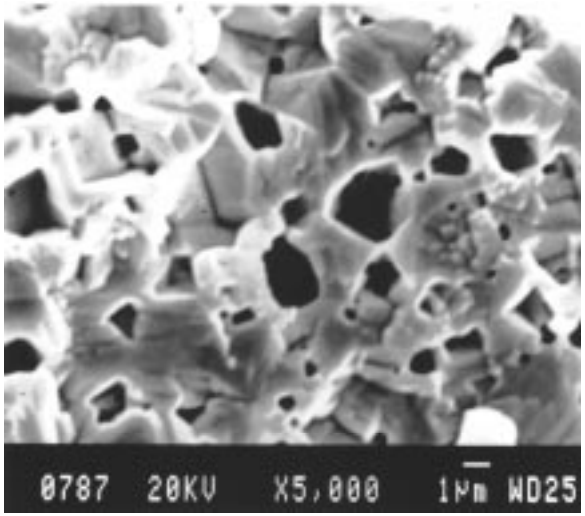
II-Part – Solid oxide fuel cells (SOFC)

Properties of SCS derived SOFC

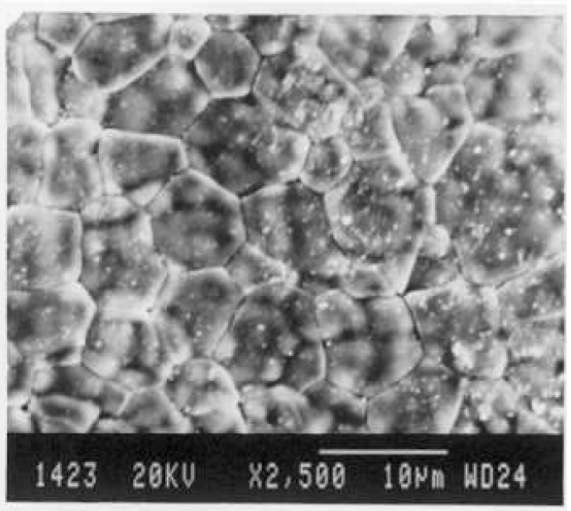
SOFC Components	Conductivity at 1173 K (S/cm)	Thermal Expansion Co-efficient at 1173 ($x10^{-6}$ K^{-1})
Cathode:		
$La_{0.84}Sr_{0.16}MnO_3$	202	12.63
$La_{0.84}Ba_{0.16}MnO_3$	156	10.91
$Pr_{0.75}Sr_{0.25}MnO_3$	114	10.20
$Nd_{0.75}Sr_{0.25}MnO_3$	140	10.70
Anode: 30 Vol% Ni/YSZ	40	11.60
Electrolyte: 8mol% YSZ	0.11	10.70
Interconnect $La_{0.8}Ca_{0.2}Cr_{0.9}Co_{0.1}O_3$	23	11.65

Microstructures of SCS SOFC powders

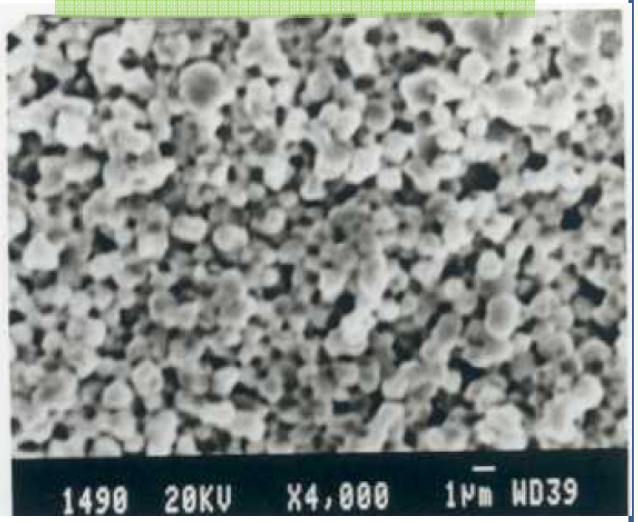
CATHODE-LSM



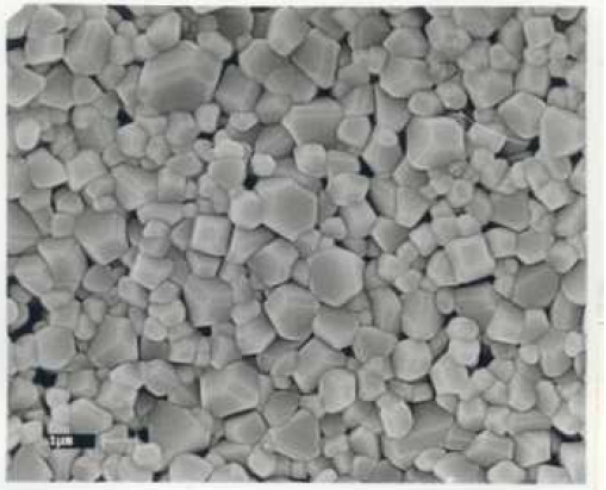
E LECTROLYTE-YSZ



Anode- NiO-YSZ



INTERCONNECT-Doped LCR



J. Mater. Chem., 1997, 7(12), 2499–2503, citations-29

S.T. Aruna et al. / Solid State Ionics 120 (1999) 275 –280, 34

S.T. Aruna et al. / Solid State Ionics 111 (1998) 45-51, Citations:125

From powders to Coatings
(2001-to date @ NAL)

Fruits of My Continued interaction with Prof. Patil

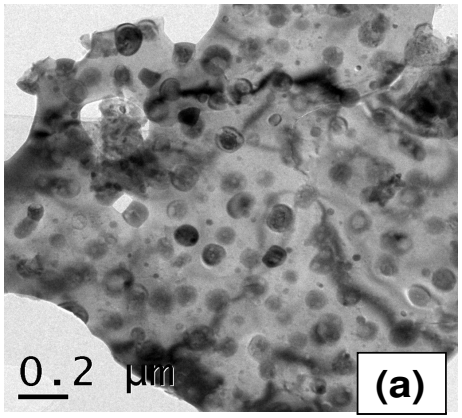
Combustion synthesis: an update
KC Patil, ST Aruna, T Mimani
Current Opinion in Solid State and Materials Science 6 (6), (2002) 507-512 390

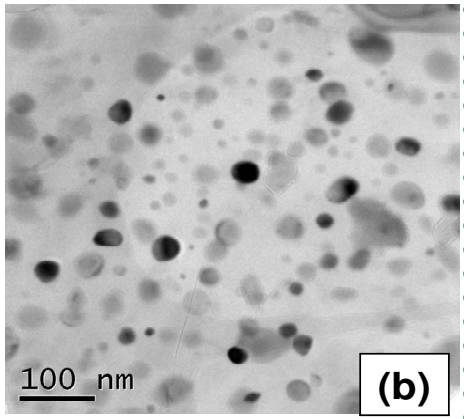
Chemistry of nanocrystalline oxide materials-Combustion synthesis, properties and applications
KC Patil, MS Hegde, T Rattan, ST Aruna
World Scientific, 2008, 132

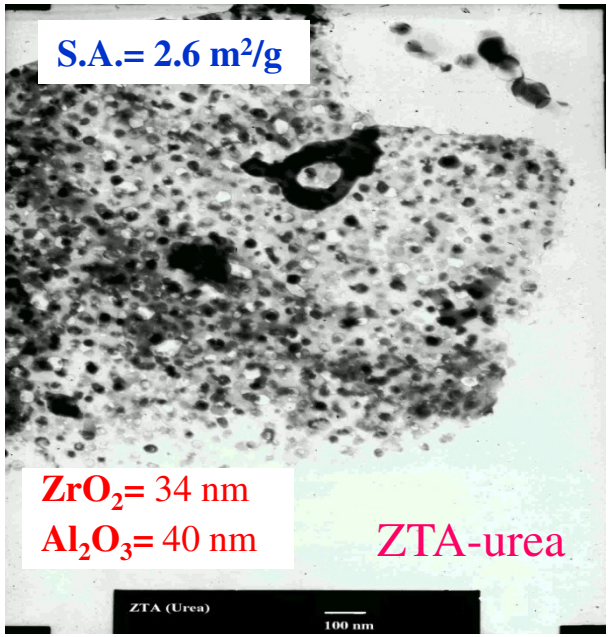
Combustion synthesis and nanomaterials
ST Aruna, AS Mukasyan
Current Opinion in Solid State and Materials Science 12 (3),2008, 44-50 159

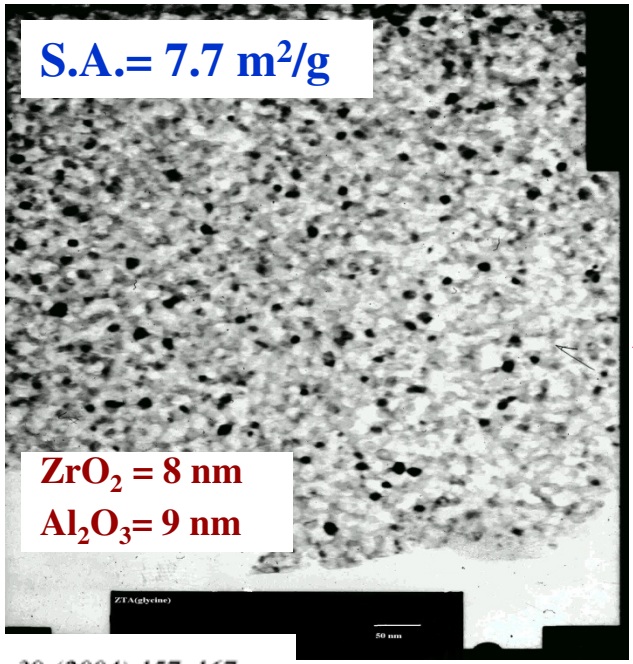
Mixture of fuels approach

- *Smaller particle size*
- *Higher surface area*
- *Lower sintering temperature*
- *Lower agglomeration*





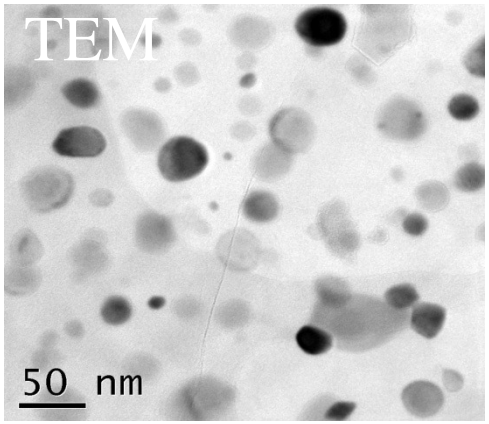


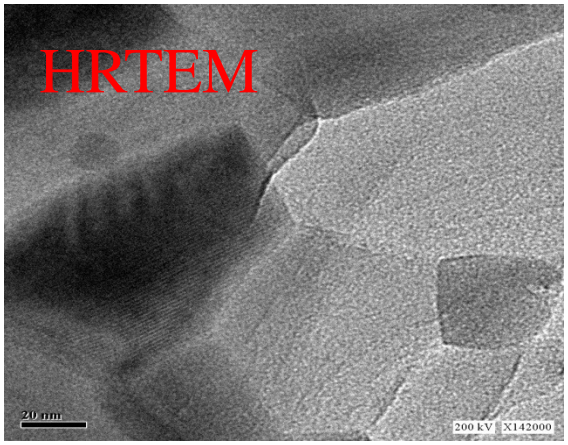


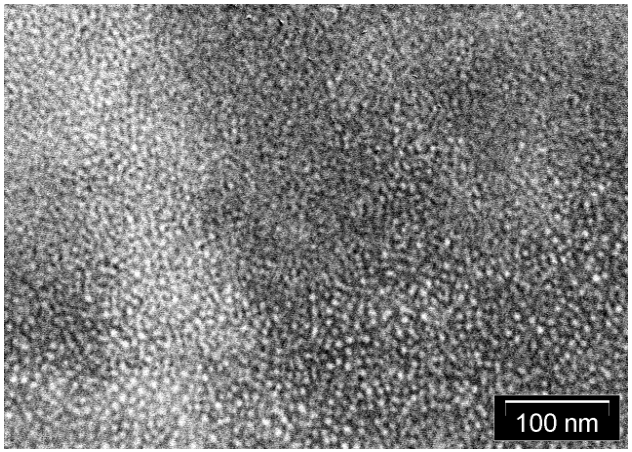
ZTA-urea+glycine+AA

S.T. Aruna, K.S. Rajam / Materials Research Bulletin 39 (2004) 157–167

Preparation of nanopowders







➢**Preparation of nanosize oxide powders – e.g. YSZ, PSZ, Al_2O_3, ZTA, YZA, CeO_2,YDC**

Novel Methodology

"Mixture of fuels approach"

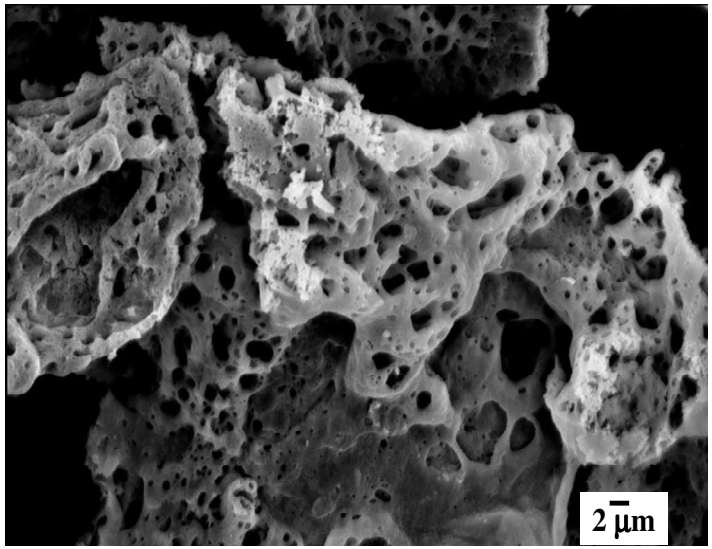
S.T. Aruna, et al. Mater. Res. Bull 39 (2004) 157-167. **(No. of times cited:83)**

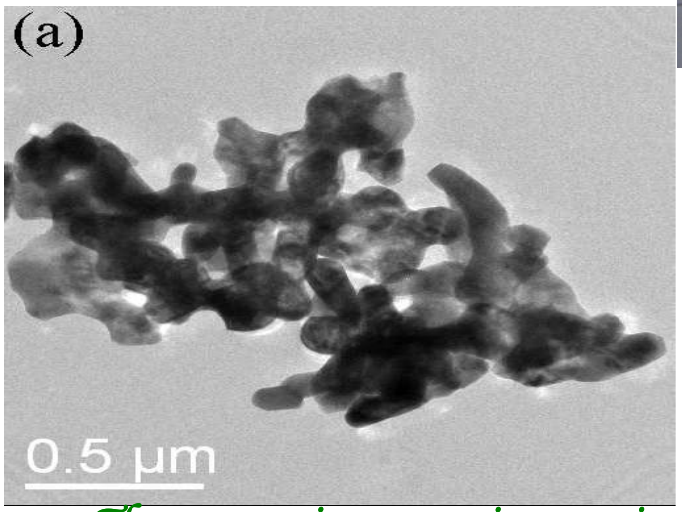
- ***decreased crystallite size***
- ***synthesis of oxides with low oxidation state***
- ***decreasing sintering temperature***

Stabilization of lower oxidation state of Ce in $CeAlO_3$

$CeAlO_3$

- **Oxide with lower oxidation state and an important catalyst**
- **Synthesized at 1350-1500°C in a reducing atmosphere using H_3BO_3 flux**





Magnetic Property

Paramagnetic (100K-300K)

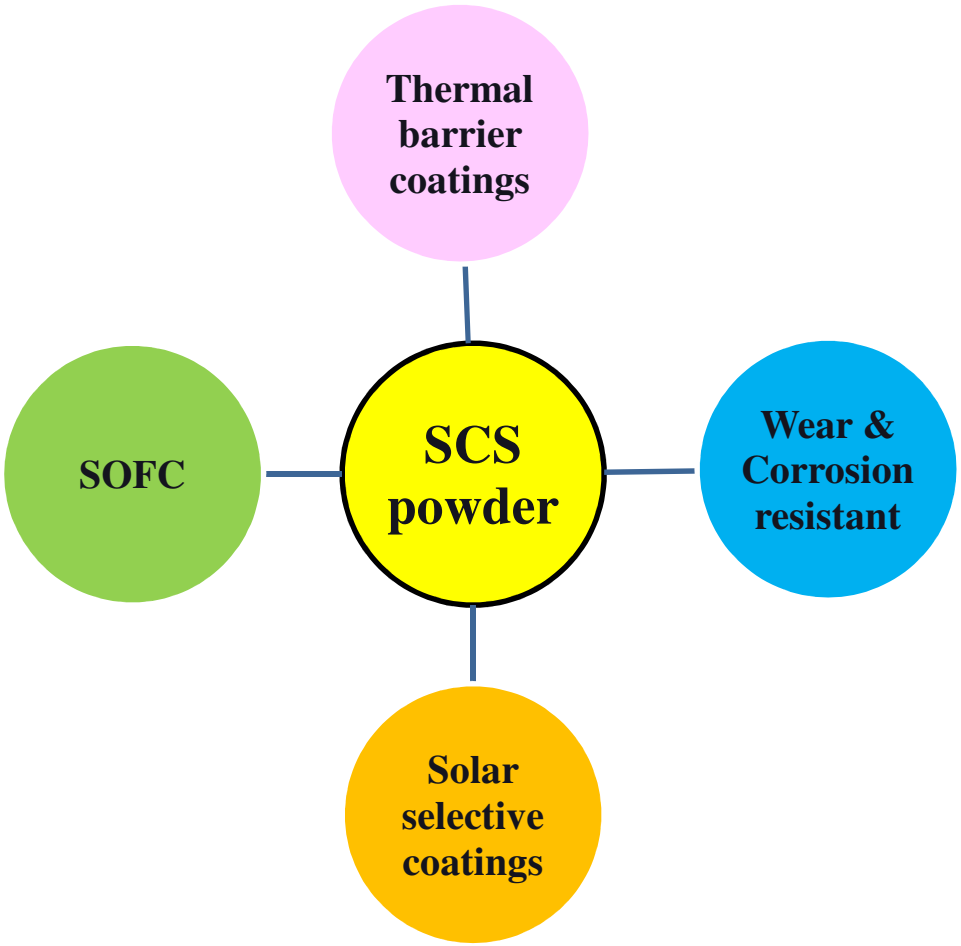
Fits Curie-Weiss model (θ_p = 40K)

μ_{eff} = 2.2 (Ce^{3+})

- *The magnetic properties are similar to that of single crystals indicating high quality of combustion synthesized $CeAlO_3$*

Materials Research Bulletin 44 (2009) 728–733. (12 times) & Material Chemistry and Physics 119 (2010) 485-489(8 times)

Applications of solution combustion synthesized powders



Electrodeposited Composite Coatings

- **When designing machine components, engineers often combine a basis metal with a surface coating to achieve the quality, economy, and reliability desired in their product**
- **Of the numerous surface treatments available, industrial hard chromium continues to be one of the most popular coatings**
- Various engineering applications - machine construction and aero-engines
- Automobile industry uses electroplated Ni/SiC for wear protection of cylinder linings and piston rings.
- Lubricant coatings for mechanical & process industries for valves, trajection molds or sliding contacts
- For corrosion protection of steel in automobile industry
- Composite coatings are produced by direct entrapment of solid particles during the build-up of the metal matrix
- The properties of the coatings are governed by the type and size of the particle, its content in the coating and the mode of distribution

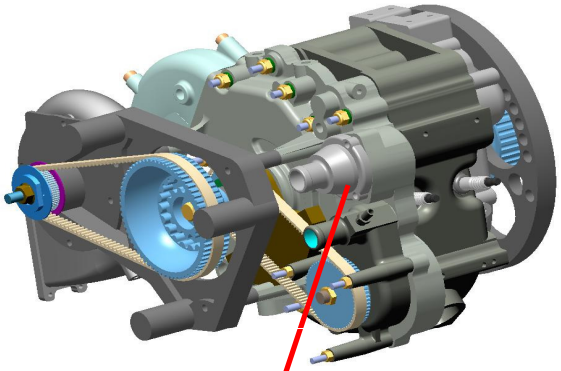
Applications of electrocomposites

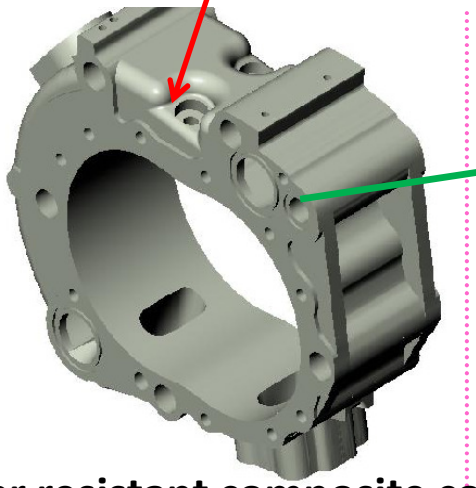
A version of TriCom, a cobalt phosphorus electro-composite coating, has been incorporated into several components for the F-35 Lightning II JSF aircraft.

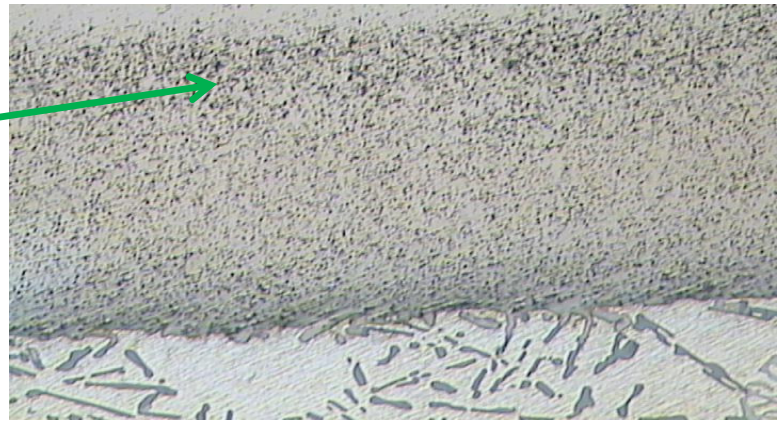
*Airbus, Boeing, and Department of Defense

Electrodeposited composite

Wear Resistant Ni+SiC coatings on the contacting faces of the trochoid housing of the Wankel Engine (UAV-NISHANT)

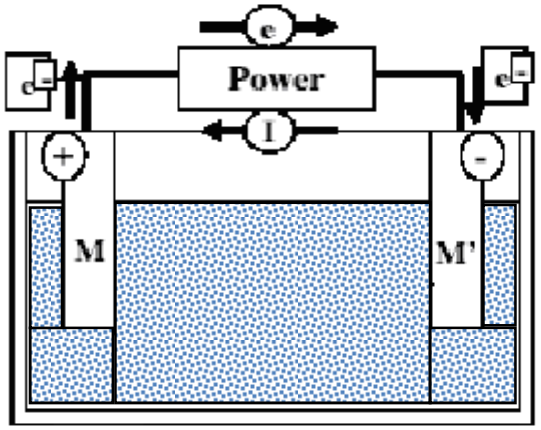




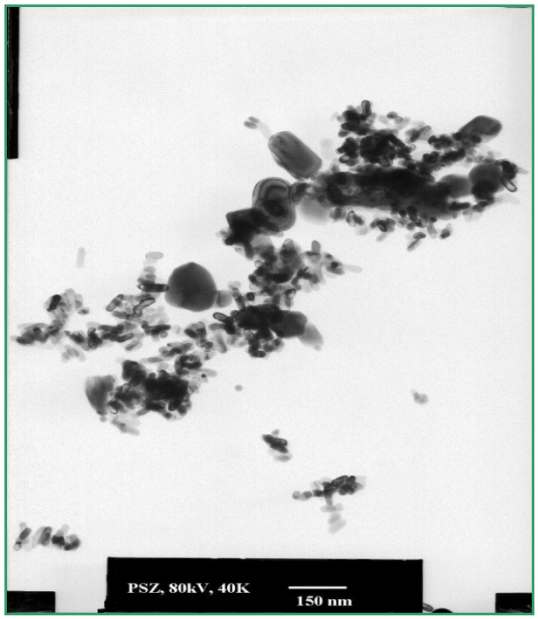


Wear resistant composite coatings for rotary and reciprocating engines in light weight aircrafts, UAVs, micro UAV, automobiles etc.

Electrodeposition



- *50 g/L Ni (300 g/L Nickel sulfamate)*
- *10g/l nickel chloride*
- *30 g/l boric acid*
- *0.2 g/L 10% sodium lauryl sulphate*
- *Temperature: RT*
- *PH:4*
- *Substrate:brass (2.5 cm×3.75 cm)*
- *Current density:* 0.23 A/dm^2 for 20 h, 0.77 A/dm^2 for 6 h,1.55 A/dm^2 for 3 h and 3.1 A/dm^2 for 1.5 h



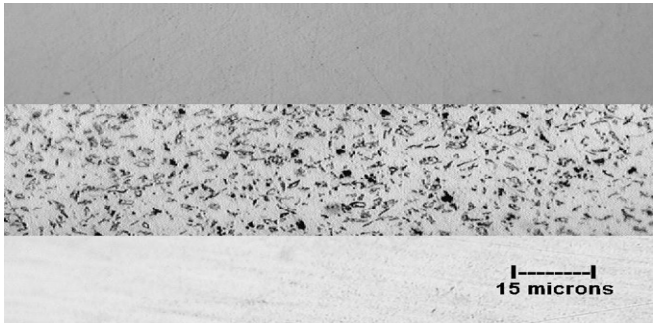
Particles studied: PSZ, YSZ, Al_2O_3, ZTA, AZY, CeO_2, YDC, etc

Advantages

- *The required oxide powders are synthesized in-house.*
- *Readily available chemicals are used.*
- *The process is simple and fast and does not require high temperature calcination.*
- *The process has been scaled up to prepare 150 g/batch.*

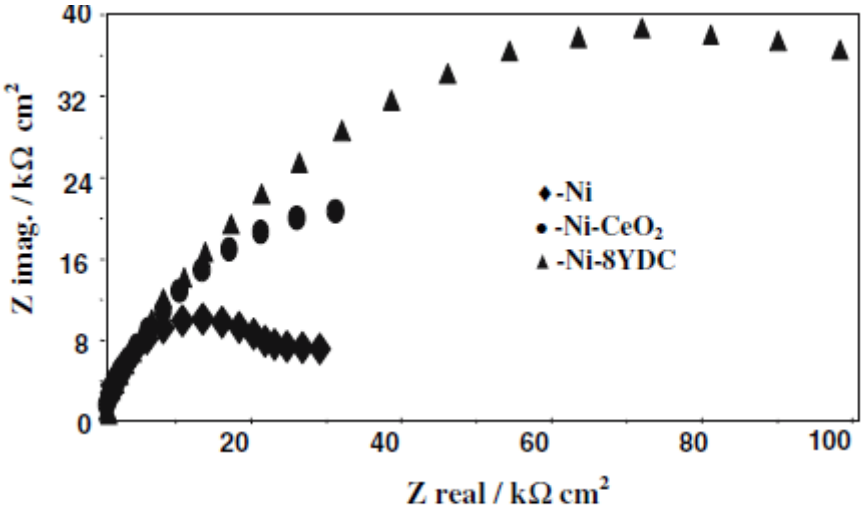
Vickers Hardness

Ni/YSZ (10 nm) = 563-618
Ni/PSZ (30 nm) = 410-430

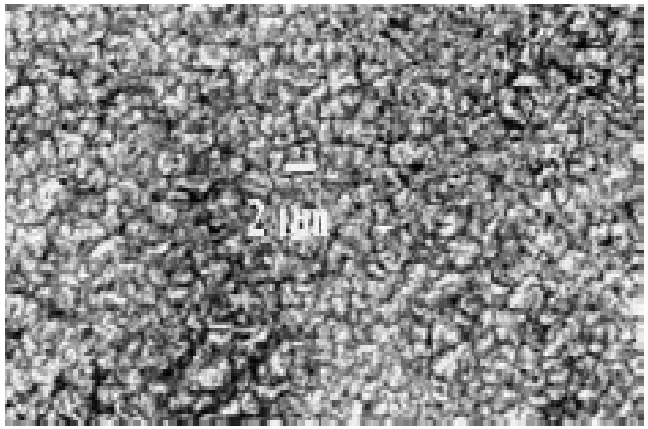


Scripta Materialia 48 (2003) 507–512 citations 31

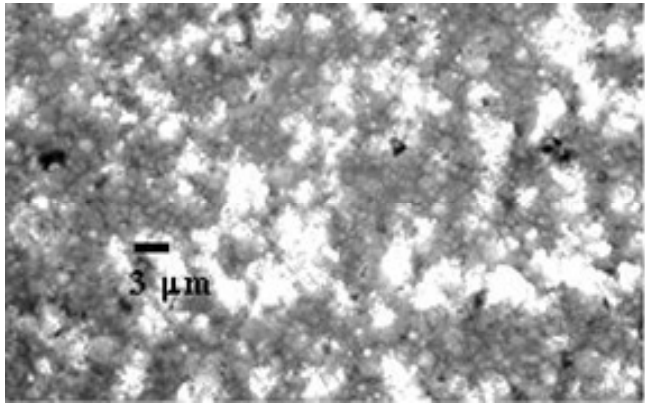
Ni-Ceria & Ni-YDC



Ni



Ni-YDC

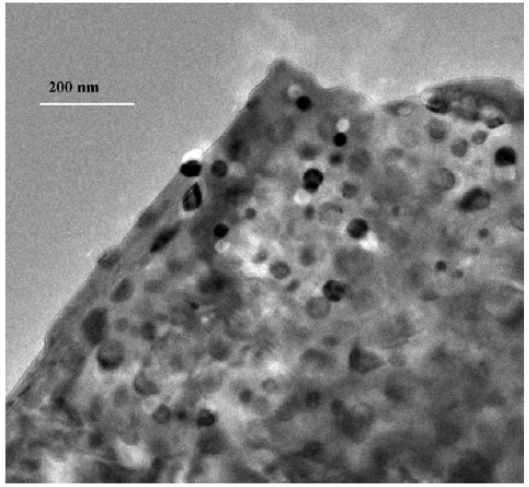


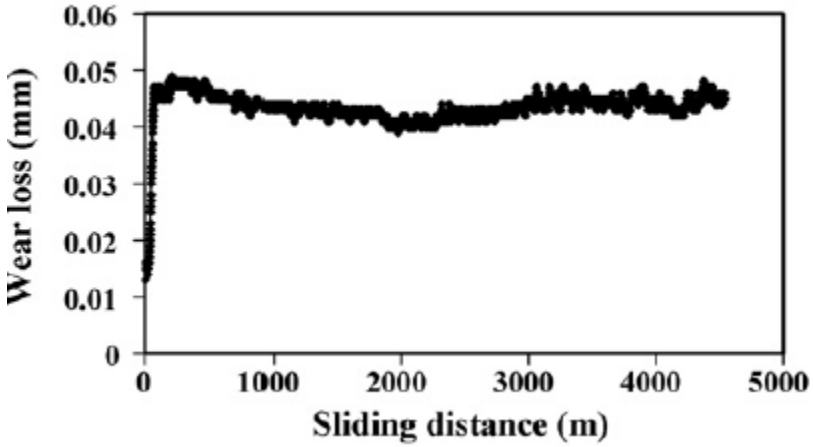
Sample	i_{corr} ($\mu A\ cm^{-2}$)	E_{corr} (V)	b_c ($V\ dec^{-1}$)	b_a ($V\ dec^{-1}$)	R_p ($\Omega\ cm^2$)
Ni	0.61	–0.298	0.078	0.130	35,940
Ni–CeO_2	0.26	–0.285	0.068	0.107	60,340
Ni–8YDC	0.16	–0.284	0.108	0.079	1,18,000

- Surface Coatings and technology, 200 (2006) 6871-6880 ((No. of times cited:65)
- Journal of Applied Electrochemistry, 37 (2007) 991-1000 (No. of times cited:9)

Ni-ZTA and Ni-YZA

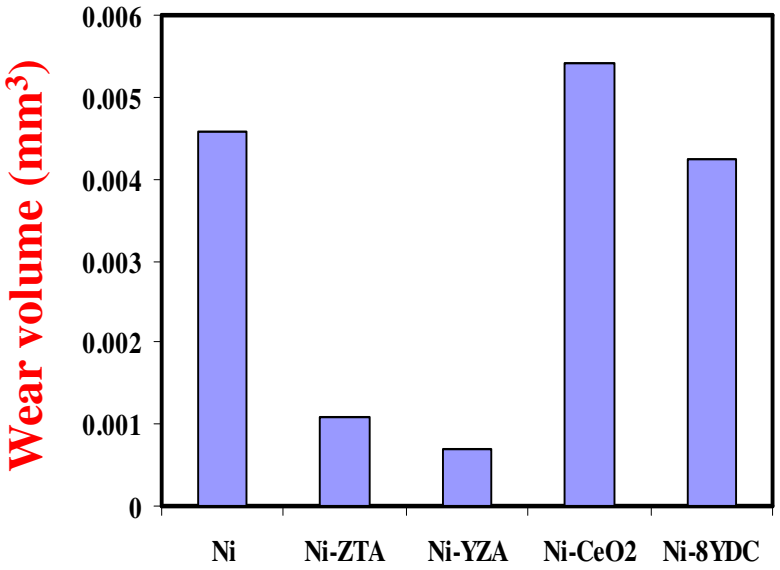
Sample	Knoops hardness (50 gf)	Total loss of height (μm)	Wear volume (mm^3)	Coefficient of friction	I_{corr} ($\mu A/cm^{2)}$
Ni	389	18	$4.57x10^{-3}$	0.517	0.6759
Ni-ZTA	549	9	$1.11x10^{-3}$	0.606	0.8634
Ni-YZA	546	7	$0.7\ x10^{-3}$	0.457	0.3782



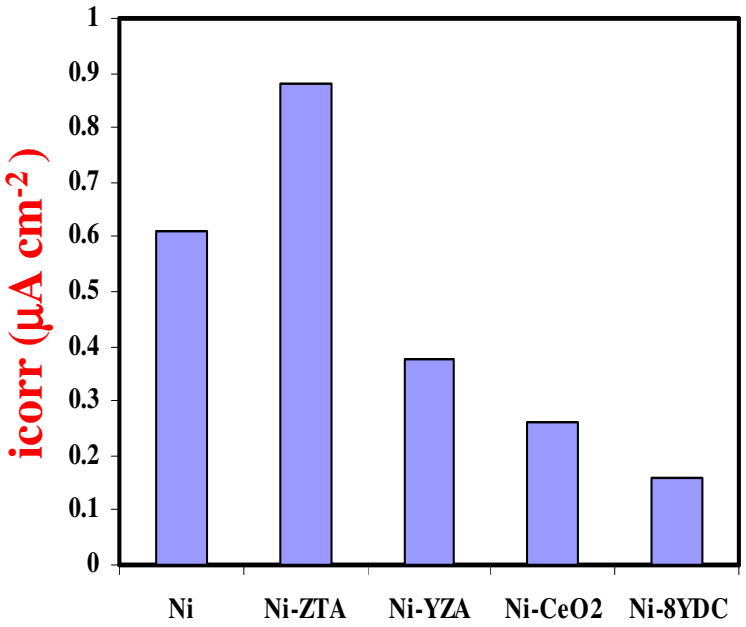


Journal of Alloys and Compounds 468 (2009) 546–552 (No. of times cited:37)
Indian patent no. IN254523 Granted date: 12/11/2012,
ST Aruna, et al Surface engineering 21 (3), 209-214, citations:15

Comparison of wear & corrosion resistance properties of Ni composites



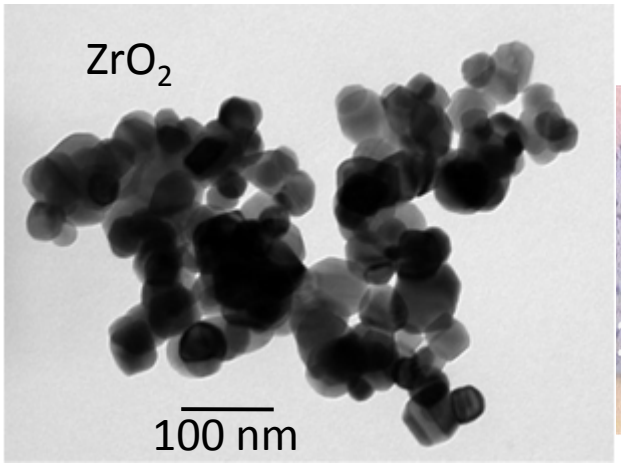
Wear resistance



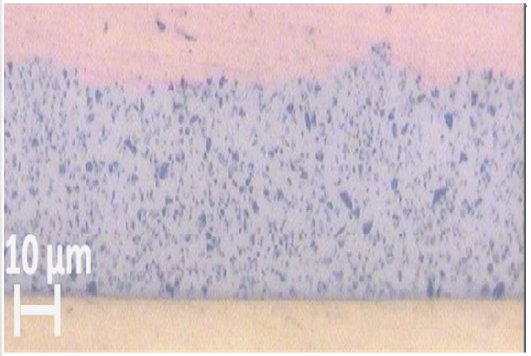
Corrosion resistance

- **Wherever engineering components undergo wear and corrosion problems, Ni-YZA may be used**
- **Ni-YZA is also cost-effective**

Multifunctional properties of electrodeposited Ni-composite coatings



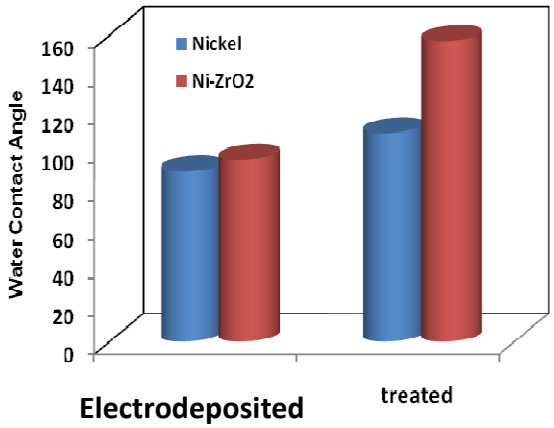
Ni-ZrO_2



Corrosion resistance

- **5 times improvement over Ni**
  (I_{corr}-0.16 vs. 0.85 µA/cm²)
- **2400 hours salt spray test**

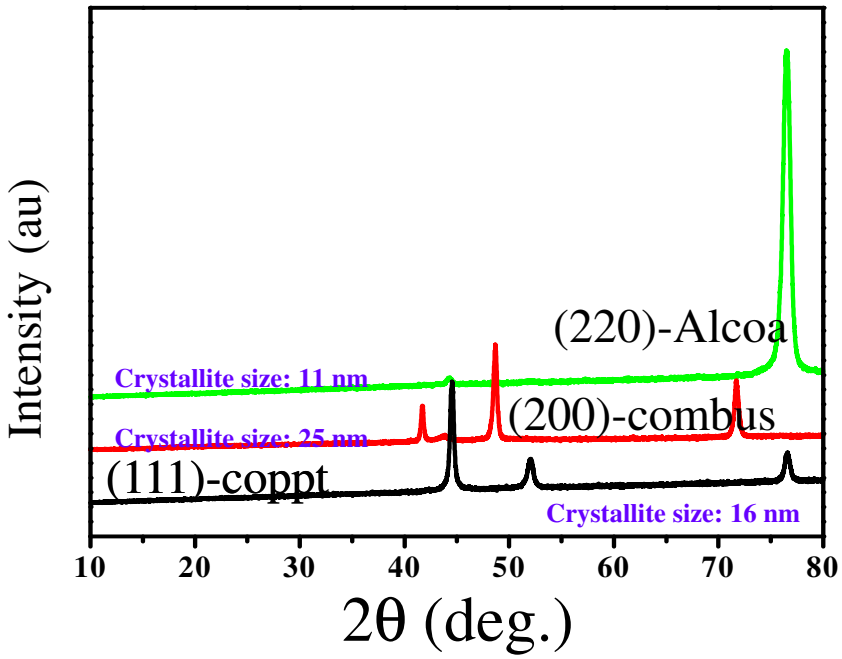
Microhardness ~ 800 HK (50 gF)

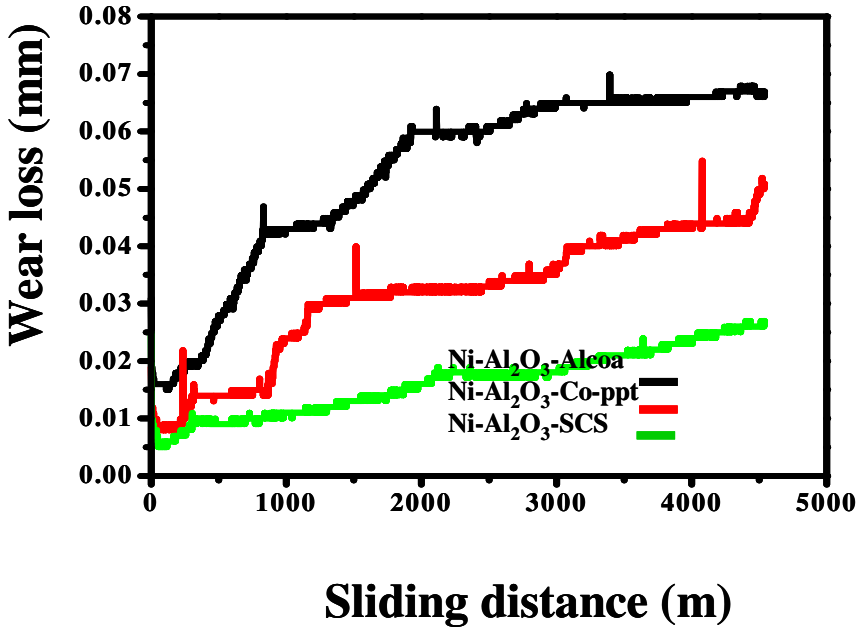


Wear resistance (2 orders of magnitude)

Coating	Wear rate (mm^3/Nm)	Average COF
Ni	$5.50x10^{-5}$	0.78
Ni-SiC	$1.35x10^{-5}$	0.75
Ni-ZrO_2	$6.60x10^{-7}$	0.50

$Ni-Al_2O_3$ composite coatings

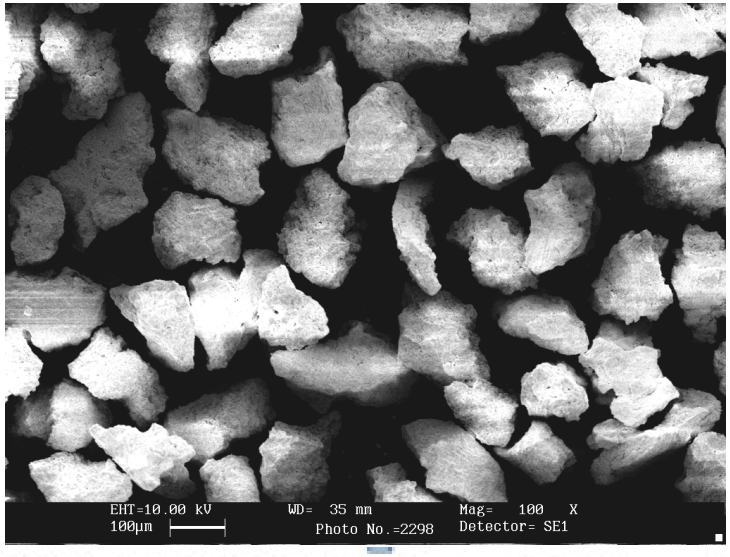


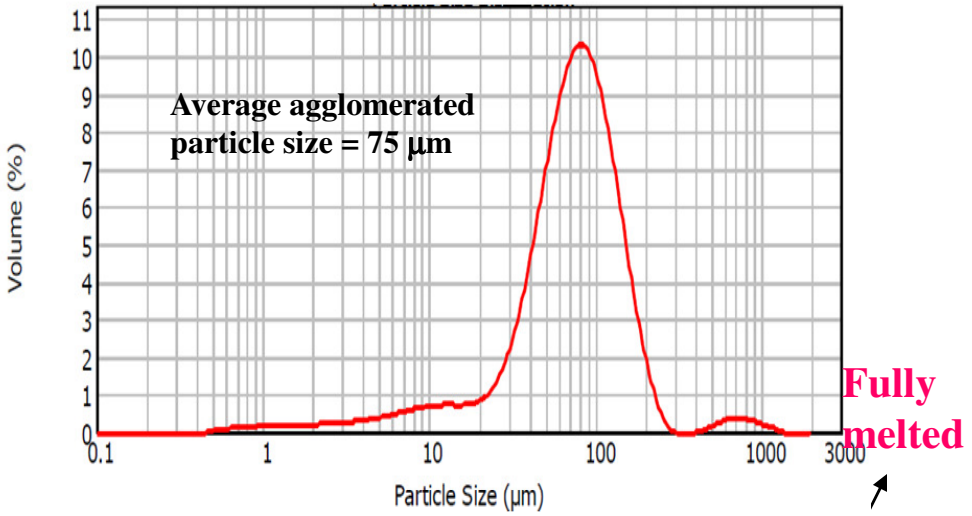


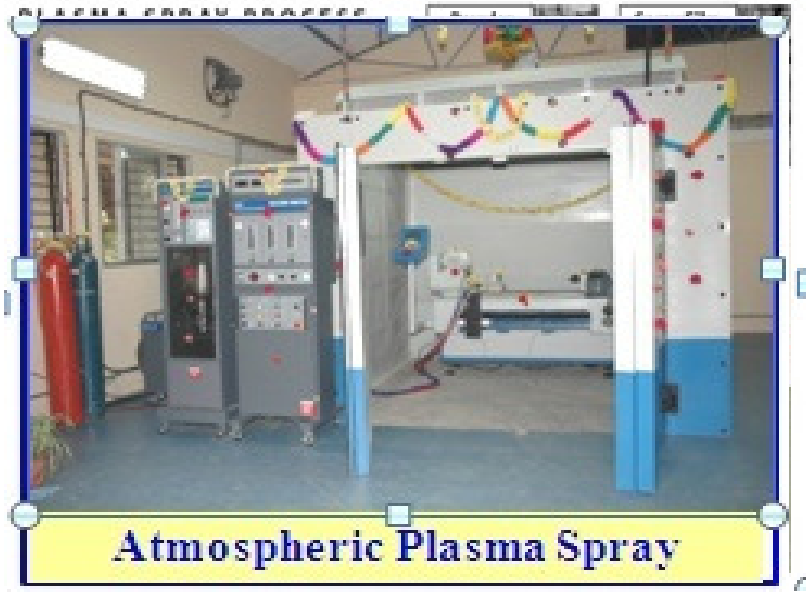
Sample	i_{corr} ($\mu A/cm^2$)	E_{corr} (V)	R_p ($k\Omega\ cm^2$)	R_{coat} ($k\Omega\ cm^2$)	R_{ct} ($k\Omega\ cm^2$)
Ni	0.6267	-0.451	4.82	4.35	1.92
$Ni-Al_2O_3-\alpha$ (SCS)	0.0242	-0.242	92.89	105.6	109.3
$Ni-Al_2O_3-\gamma$ Co-ppt	0.0119	-0.184	131.5	155.0	164.5
$Ni-Al_2O_3$-Alcoa	0.0839	-0.267	42.2	42.0	46.8

J. Applied Electrochemistry 40 (2010) 2161–2169. J. Applied Electrochemistry 41 (2011) 461–468.

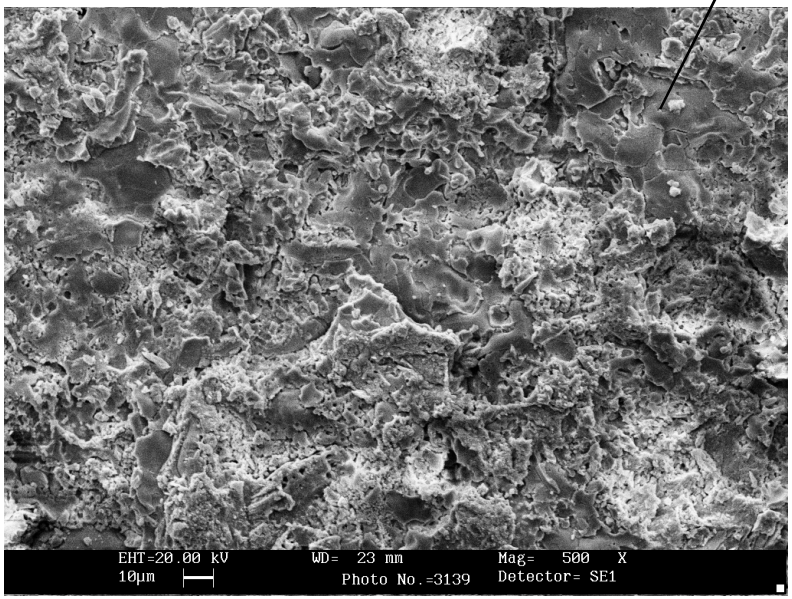
Plasma sprayable $La_2Zr_2O_7$ powder for TBC Application





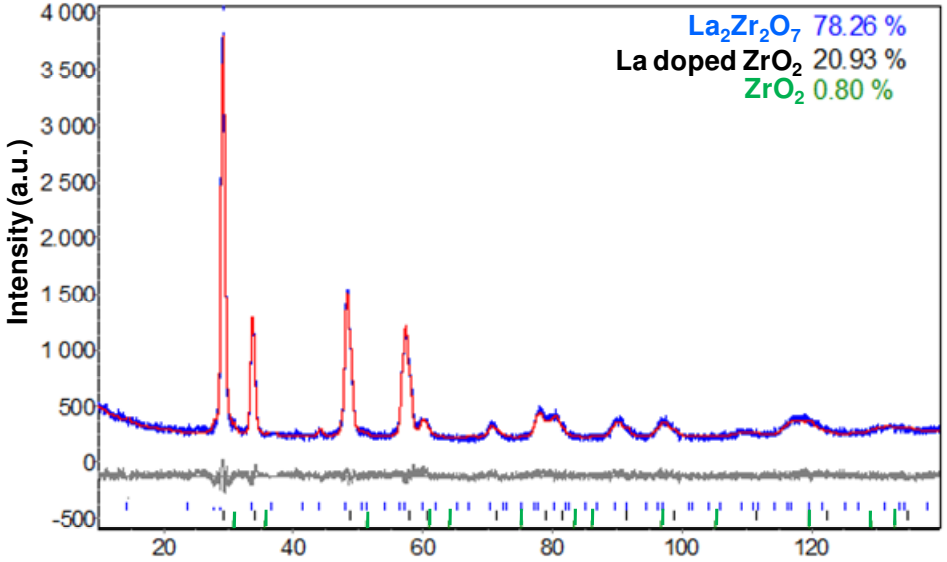


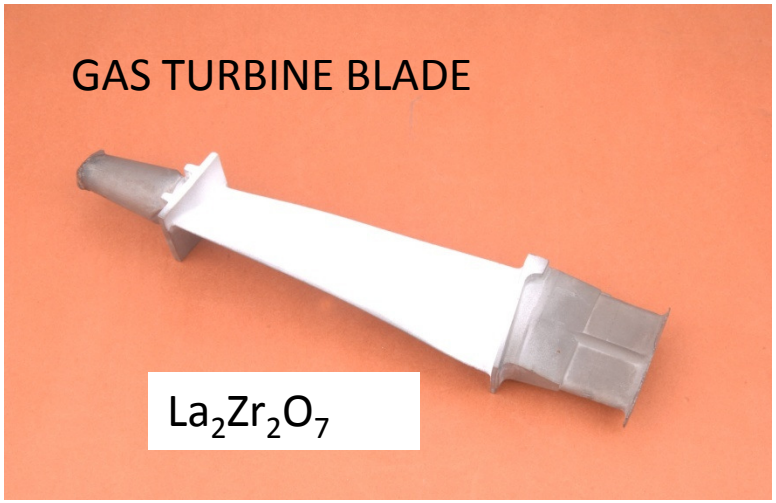
Fully melted

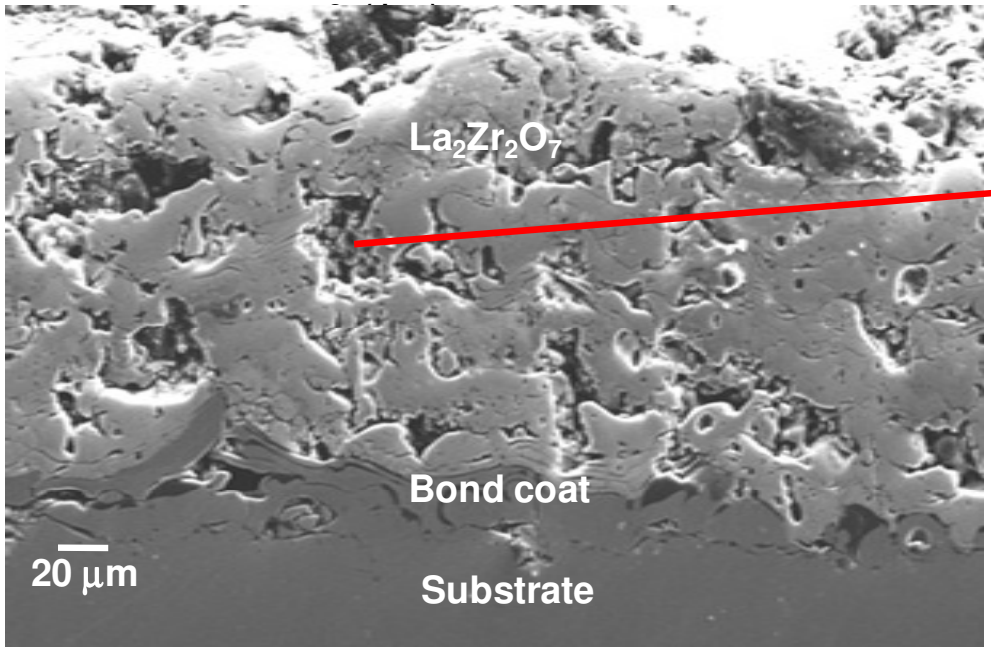


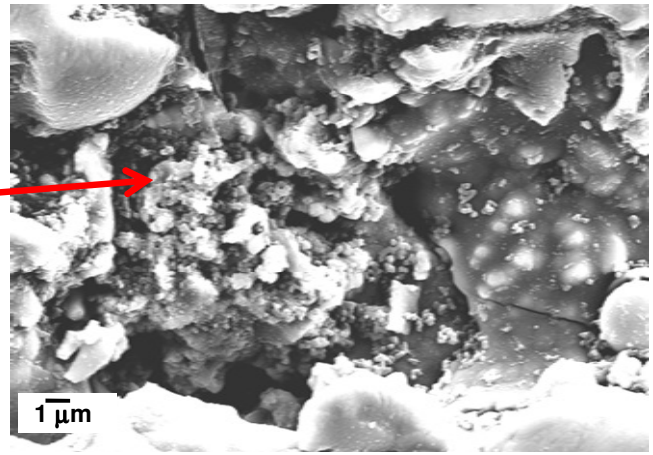
Bimodal distribution

Properties of $La_2Zr_2O_7$ Coating







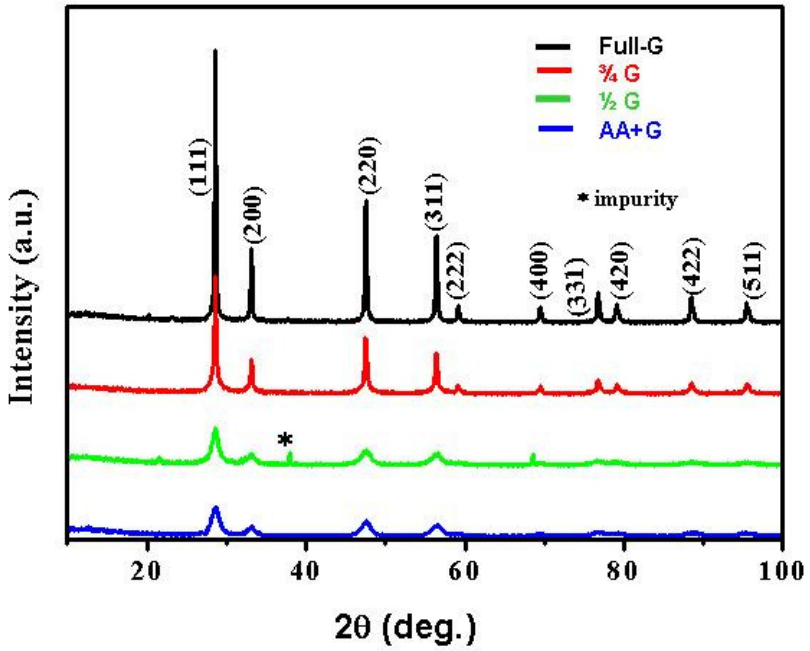


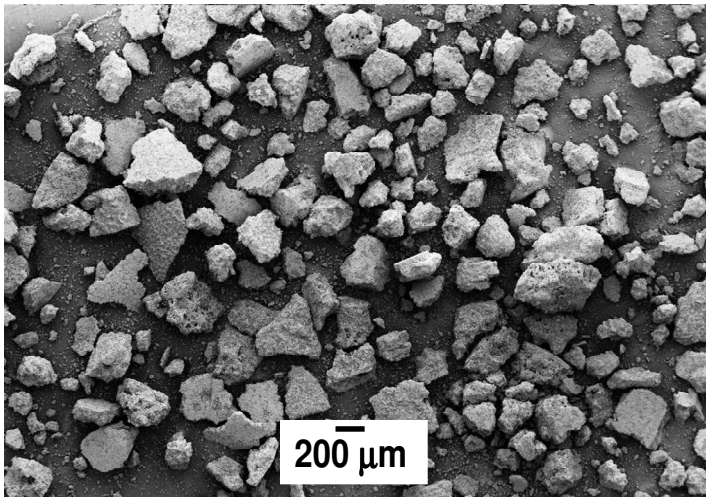
•$La_2Zr_2O_7$ coating exhibited a thermal conductivity value of 1.08 $Wm^{-1}K^{-1}$ at 900 °C

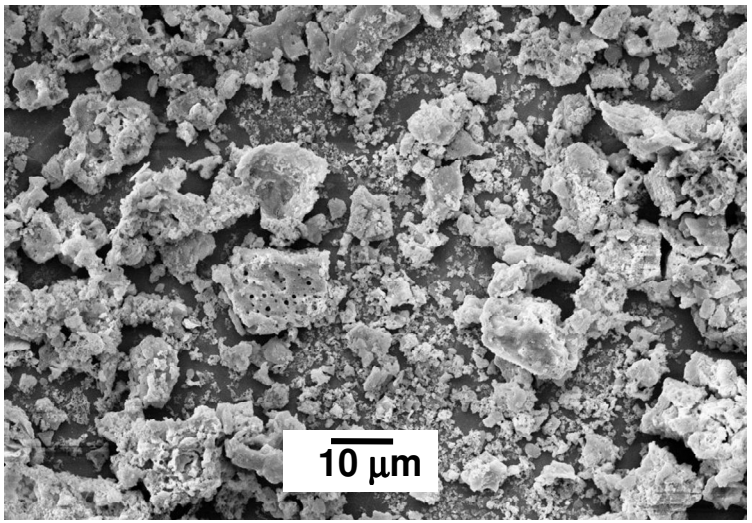
Surface & Coatings Technology 219 (2013) 131–138.

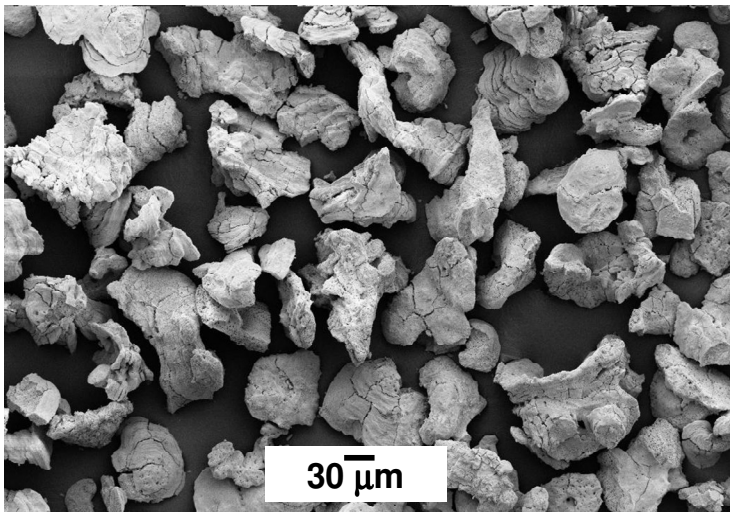
Solution combustion approach for the preparation of plasma sprayable powders

- **Ceria : interlayer in SOFC**



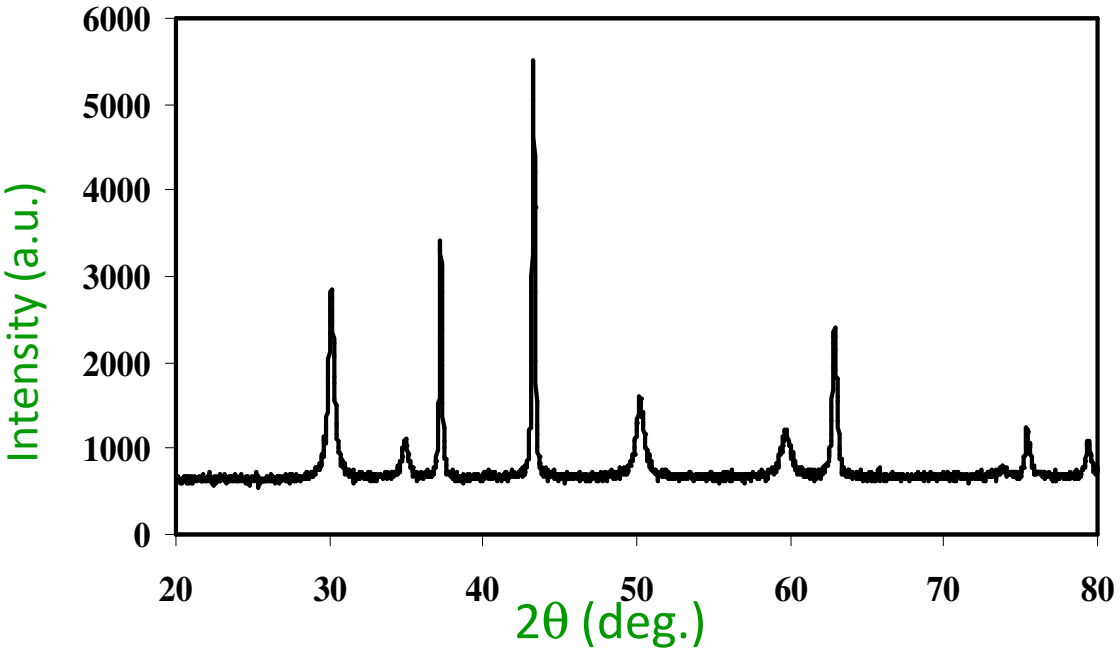






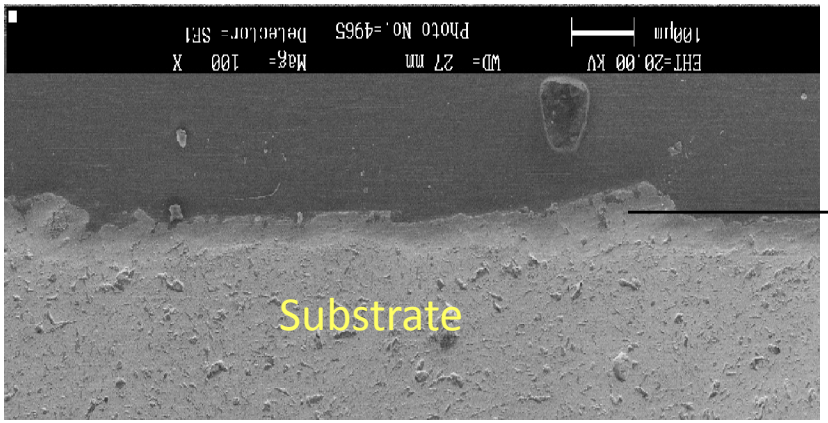
Ceramics International 35 (2009) 1353–1355.

Plasma sprayable NiO-YSZ anode powder for SOFC



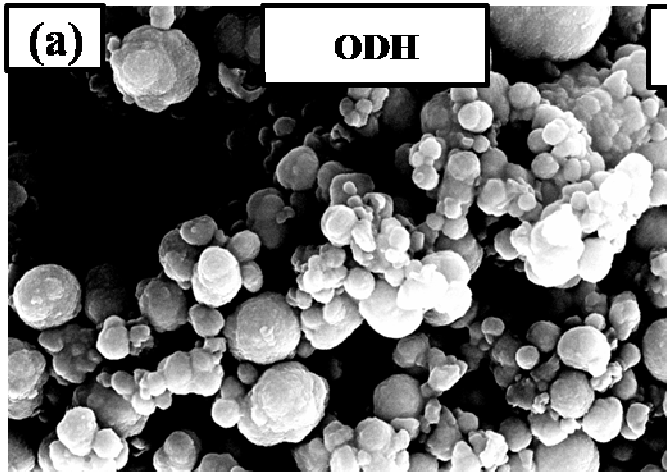
Average agglomerated particle size = 10 µm

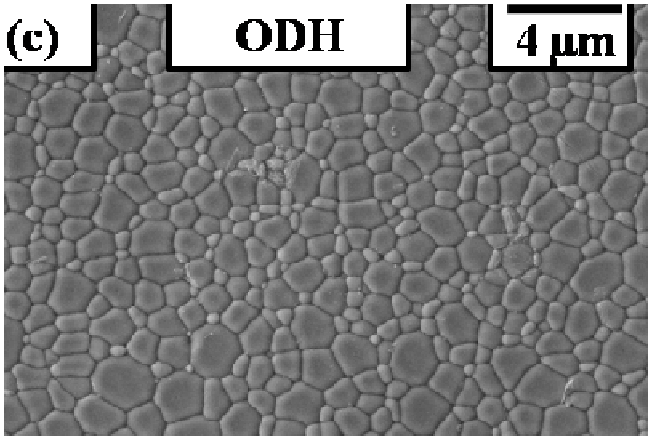
Flowability = 40s/50g

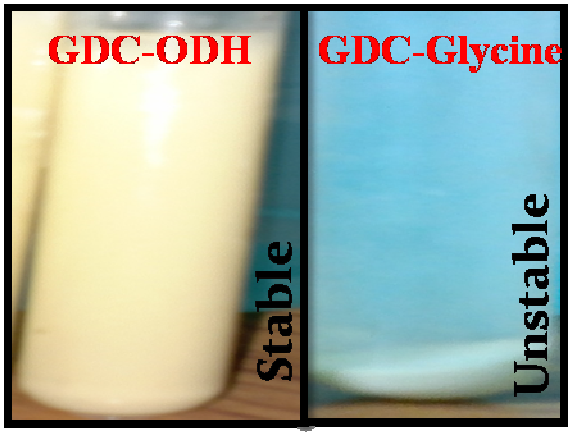


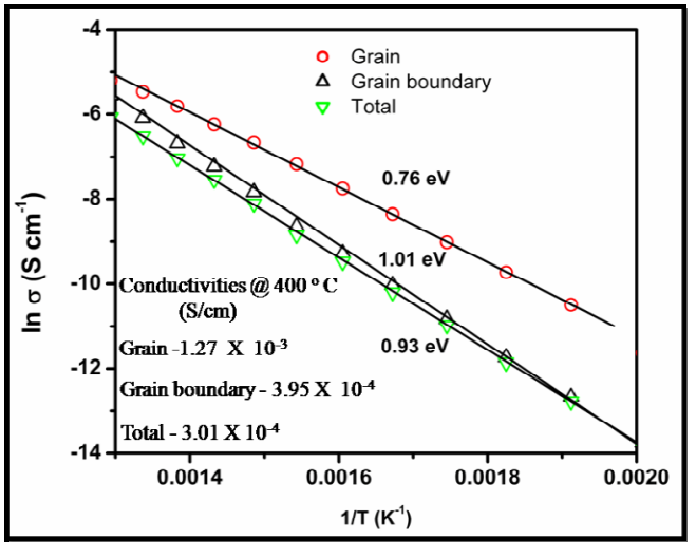
Anode coating

8 mol% Gd_2O_3 doped ceria for wet-spray & brush painting



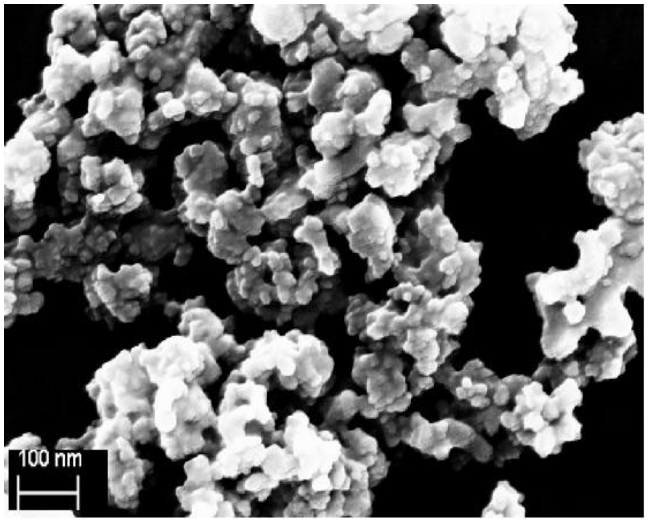


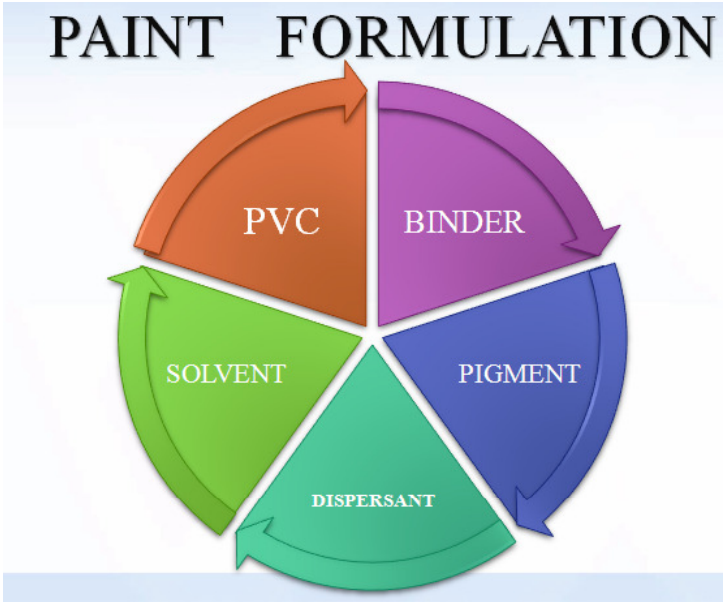




Journal of Power Sources 214 (2012) 358-364

POLYMER BASED SOLAR SELECTIVE PAINT COATING CONTAINING SCS BLACK PIGMENT





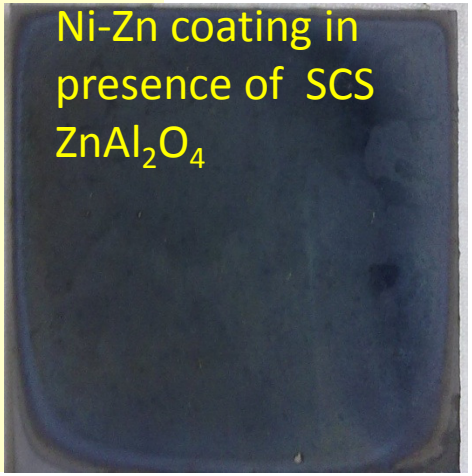
PDMS BASED COATING

SCS Powder:

α= 0.913 & ε = 0.41

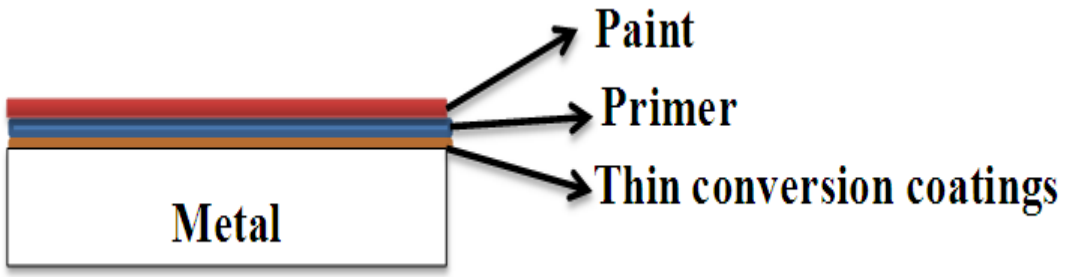
Commercial Powder:

α= 0.915 & ε = 0.52

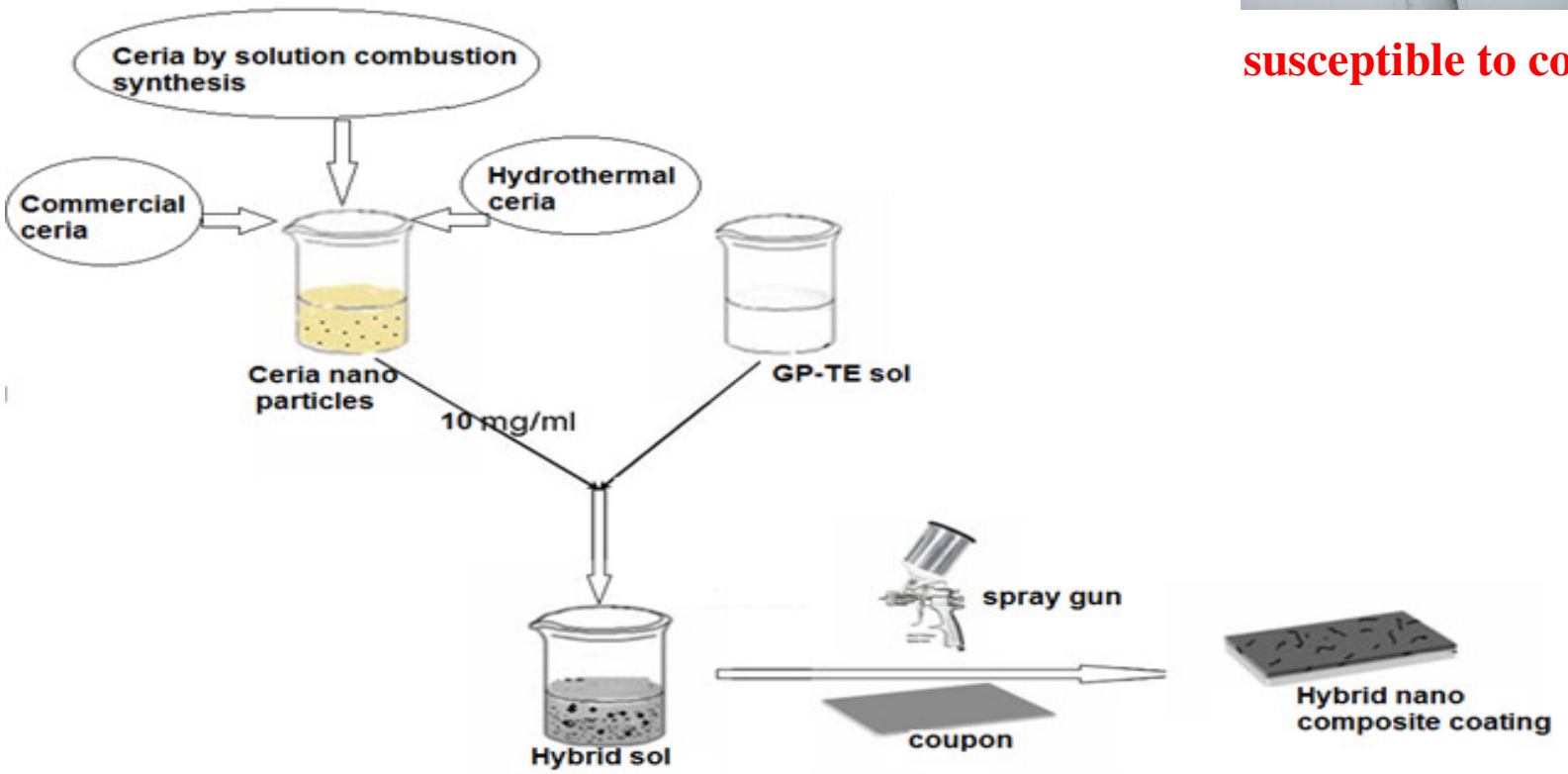


α= 0.927 &
ε = 0.16

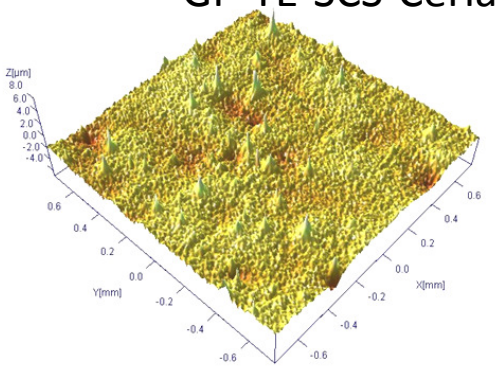
Eco-friendly sol-gel based pretreatments for AA2024

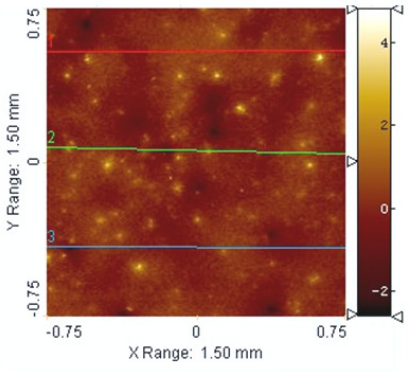


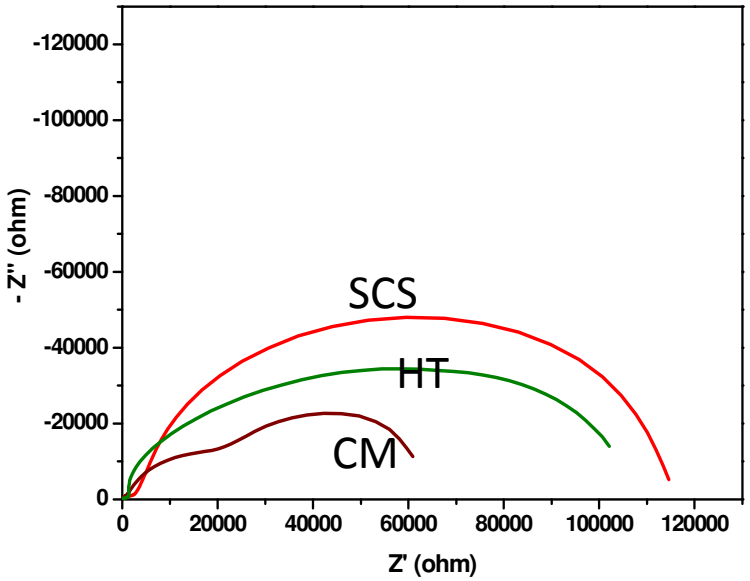
susceptible to corrosion



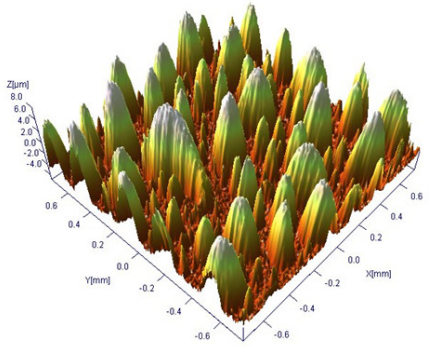
GP-TE-SCS-Ceria

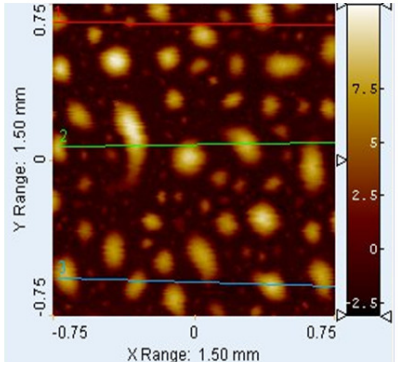






GP-TE-CM-Ceria





GP-TE-CeO_2-SCS

GP-TE-CeO_2-HT

GP-TE-CeO_2-CM

CONCLUDING REMARKS

- Solution combustion method is a versatile method for the preparation of oxide powders

- Solution combustion synthesized powders can be used in the development of a variety of functional coatings

- Solution combustion method is a Pandora`s box. It is a challenge for researchers to explore it.

Acknowledgements

- Prof. K.C. Patil
- Director & Head SED, NAL
- CTSM & NMITLI (CSIR) – for funding
- N. Balaji, NAL
- My collaborators
- Mr.V.K.W. Grips, NAL
- Mrs. Ezhil Selvi, NAL (corrosion studies)
- Project trainees
- Muniprakash, Manikandanath, Mr. Siju


Thank You